En Chem, Inc.

Quality Assurance Document

SET No: 1

Standard Operating Procedure
Analytical Method

TITLE: Analysis of Polychlorinated Biphenyls (PCB's) by Gas Chromatography

DEPARTMENT: Semivolatile Organics

APPLICATION: This method is used to determine the concentration of PCB's in water soil and biological samples. The following PCB Aroclors are routinely analyzed using this method:

Aroclor 1016	Aroclor 1232	Aroclor 1248	Aroclor 1260
Aroclor 1221	Aroclor 1242	Aroclor 1254	

REFERENCES: Test Methods for Evaluating Solid Waste, 3rd. Ed.
SW846 method 8000B, December 1996
SW846 method 8082, December 1996

PROCEDURE SUMMARY:

A volume of sample extract is injected into a gas chromatograph (GC) and compounds in the effluent are detected by an electron capture detector (ECD). Results are reported in parts per billion (µg/kg or µg/L). Soil and sediment sample results are corrected for moisture and reported on a dry weight basis. Biological results are reported based on wet weight or, "as is".

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SAFETY PRECAUTIONS:

- The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

- PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood.

SAMPLE PREPARATION:

Prior to utilizing this analytical method, liquid samples are extracted using Method 3510C or 3520C. Soil and sediment samples are extracted using Method 3540C or 3550B. Biological samples are extracted using Method 3540C. A variety of cleanups may be performed as determined necessary. A column chromatography cleanup using Florisil (En Chem Method SVO-57) typically separates the Aroclors from most other typical environmental interference's in any of the matrices. Soil and sediment samples typically need to have sulfur removed using elemental mercury (En Chem Method SVO-27) or by gel permeation chromatography (En Chem Method SVO-26). A sulfuric acid cleanup may be used, as required, to further remove contaminants (En Chem Method SVO-28).

SAMPLE EXTRACT HANDLING AND STORAGE

Sample extracts must be analyzed within 40 days from the date of extraction.

APPARATUS AND MATERIALS:

Note: Equivalent apparatus and materials to those listed may be used.

Gas Chromatograph:	Hewlett Packard (HP) 5890 equipped with Electron Capture Detectors (ECD)
GC Autosampler:	HP7673A.
Data Processor:	TurboChrom IV.
Printer:	HP laserjet 4M/Plus.
Syringes:	10-1000 µL Gastight syringes (Hamilton series 1000.
Autosampler Vials:	2 mL with crimp top caps.
Detector:	ECD (HP).

GC Columns:

Column 1 - DB-17 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

Column 2 - DB-1701 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

Column 3 - DB-5 Capillary column, 30 m x 0.32 mm I.D. (J&W Scientific).

Column 4 - DB-608 Capillary column, 30 m x 0.53 mm I.D. (J&W Scientific).

GC Column Conditions: Carrier gas - Helium
Flow rate - 2.0 mL/min.
Make-up gas - Nitrogen
Flow rate - 65 mL/min.
Detector temp. -350° C
Injector temp. - 205° C
Splitless injection

GC Temperature Program:
Initial temp. - 110° C
Initial time - 0.5 min.
Rate (1) - 20° C/min.
Hold Time (1) - 0.0 min.
Rate (2) - 11° C/min.
Final temp. - 280° C
Final time - 10 min.

REAGENTS:

Solvents: Hexane, acetone, and isooctane (2,2,4-trimethylpentane) pesticide grade.

Stock Standards Solutions: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 1 year from the date of preparation.

Calibration Standards: Prepare a five point curve for AR1016 and AR1260. These may be combined in the same solution (AR1660). Recommended concentrations are 0.1, 0.3, 0.5, 0.8, and 1.0 ug/mL. Prepare solutions of the remaining Aroclors at the mid-point level of the AR1660 curve. Shelf-life of the calibration solutions is 6 months from the date of preparation.

Surrogate Standards: Commercially prepared standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 6 months from the date of preparation.

INITIAL CALIBRATION:

Primary Column

The initial calibration includes analysis of five point calibration curve of a mixture of Aroclors 1016/1260 at concentrations of 0.1, 0.3, 0.5, 0.8, and 1.0 µg/mL. The Aroclor 1016/1260 calibration curve will also include TCX and DCB at concentrations of 0.01, 0.02, 0.05, 0.1, and 0.15 µg/mL. Inject a single point standard of Aroclors 1221, 1232, 1242, 1248, and 1254 at 0.5 µg/mL. Five or more peaks are selected for each Aroclor, 1016 and 1260. The calibration factor for each of the five peaks is calculated, as shown below, for each of the five levels. Calculate the %RSD for each Aroclor peak using all five calibration points. See Calibration Curve Criteria below.

Other calibration ranges may be substituted to meet expected concentrations of samples being analyzed. If only a select list of Aroclors are being analyzed for, then a five point calibration of only the Aroclors of interest may be substituted for the Aroclor 1016/1260 mixture.

The analyst will pick at least five (three for Aroclor-1221) of the largest peaks for each Aroclor for use in quantifying the samples. The peaks chosen for quantitation should have minimal co-elution with peaks of other Aroclors.

Confirmation Column

Confirmation is generally required using a second GC column of dissimilar stationary phase, or by GC/MS. When simultaneous analysis is performed for confirmation, the same initial and continuing calibration criteria apply.

Since Aroclors provide distinct multiple peak patterns which may be identified by an experienced analyst, and because the identification of an Aroclor is based primarily on this pattern recognition, the need for second column confirmation is not required for sites having a **single** Aroclor. In this case the analyst must document in the raw data the absence of major peaks representing any other Aroclor.

Calibration Curve Criteria: **All Initial calibration and calibration verification criteria apply to both analytical columns when applicable.**

1. Linear Calibration using Average Calibration Factors.

$$CF = \frac{\text{Peak Area}}{\text{Std. Concentration in ug/mL}}$$

The percent relative standard deviation (%RSD) of the five calibration factors for eachpeak, in each Aroclor, 1016 and 1260, must be less than or equal to 20%. If this is the case then linearity can be assumed, and the average calibration factor can be used in place of the calibration curve. If the %RSD is greater than 20%, a calibration curve must be used for quantitation.

2. Calibration alternatives

a. Linear Calibration.

A linear regression is used for a linear equation of the type, y=ax+b. The intercept should **not** be forced through the origin. The regression calculation will generate a correlation coefficient "r". In order to be used for quantitative purposes the r value must be greater than 0.99.

RETENTION TIME WINDOWS:

Retention time windows are generally not applicable to Aroclor analysis since pattern recognition is used to identify the types of Aroclors present. Retention time windows are calculated on each instrument when a new GC column is installed. Additional guidance is provided in method 8000.

1. Make at least three injections all analytes of interest over a 72 hour period.

2. Record the retention time for each selected peak for multi-component analytes, to three decimal places. Calculate the mean and standard deviation for each peak.

3. The width of the retention time window is defined as ± 3 standard deviations of the mean established . The minimum retention window will be ± 0.03 minutes.

4. Establish the center of the RT window for each analyte and surrogate using the absolute RT from the calibration verification standard at the beginning of the analytical shift. Optionally, the Initial Calibration RT windows may continue to be used as long as method criteria are met. For samples run during the same shift as an initial calibration, use the RT of the mid-point standard in the Initial calibration.

CALIBRATION VERIFICATION:

Analysis of Initial Calibration Verification Standard

May be required based on Project Requirements.

In order to consider the initial calibration acceptable, an Initial Calibration Verification Standard (ICV) must be analyzed within the same time clock as the calibration curve. The ICV standard must be

from a second source stock and meet the same criteria as the Continuing Calibration Verification standard before the initial calibration may be considered valid.

Continuing Calibration Verification Standard

All samples must be bracketed by acceptable calibration verifications.

A midpoint calibration check standard is injected following every ten sample injections for calibration verification. If the response factor (area/concentration) of the check standard deviates by more than 15% of the initial average response factor, the calibration is considered out of control and analysis must be stopped.

If the ending calibration verification standard exceeds the 15% criteria on the high side (i.e. an increase in sensitivity) samples which had no Aroclors detected do not need to be reanalyzed. If the continuing calibration standard criteria is exceeded on the low side (i.e. a drop in sensitivity), then the non-positive samples must be re-analyzed because the ability to meet the detection limit is in question. **Any samples injected prior to the failing calibration which do exhibit an Aroclor pattern must be reinjected under a valid calibration.**

Perform corrective action such as injection port or column maintenance. Prior to the analysis of any subsequent samples an acceptable calibration verification must be analyzed. In the event that this cannot be achieved a new initial calibration must be performed.

CALIBRATION VERIFICATION ACCEPTANCE CRITERIA:

1. The percent difference (%D) is determined for all analytes. The %D must be within ± 15% of the calibration curve. (see below)

$$\%D = \frac{R_2 - R_1}{R_1} \times 100$$

where: R_1 = True value of standard.

R_2 = Calculated amount from succeeding analyses using the $\overline{CF}$.

The analyst should verify that the software is using appropriate values for calculations.

SAMPLE ANALYSIS

Once the Aroclor pattern has been identified, compare the responses of 3 to 10 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of

Aroclor is calculated using the individual calibration factor (single point) for each of the 3 to 10 characteristic peaks chosen for that specific Aroclor.

A concentration is determined using each of the characteristic peaks and then those 3 to 10 concentrations are averaged to determine the concentration of that Aroclor.

1. Calculations:

Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(Cf)(V_i)}$$

Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(V_t)(D)}{(Cf)(W)(S)}$$

where:
A_x = Area for selected peak.
V_t = Final volume of extract in mL (adjusting for GPC cleanup)
D = Dilution factor
Cf = calibration factor *
V_i = Initial sample volume (L)
W = Initial sample weight (kg)
S= % Solids/100

* Note: If Aroclor 1016 and/or 1260 is being quantified use the average calibration factor from the AR1660 curve. Use the single point calibration factor for other Aroclors. Surrogates are quantified based on the average calibration factors for TCMX and DCB analyzed with the AR1660 curve.

2. The method blank and LCS extracted along with the samples should be analyzed on the same instrument as the samples.

3. Surrogate recoveries must be evaluated using laboratory control limits (see appendix B). If **both** surrogate recoveries fail this criteria, re-extract the sample. One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. In the case of a dilution, the analysts discretion should be used.

If the analyst determines that the interferences could be removed by sulfuric acid cleanup and/or sulfur removal, then the analyst will perform the necessary cleanups and re-analyze the samples. The blank will also undergo the same cleanups and be re-analyzed.

QUALITY CONTROL

1. The method blank must meet the surrogate limits (see appendix B). If the blank fails this criteria, all of the associated samples, matrix spikes and laboratory control spikes will be evaluated and a corrective action will be determined.

2. If the blank contains any analyte of interest above the reporting limit (see appendix A), all of the associated samples, matrix spikes, and laboratory control spikes **must** be re-extracted unless the sample concentration is greater than 20X the amount found in the blank or the analyte is not detected in an associated sample. Note: For Wisconsin projects this criteria will be "Above the LOD".

3. If the laboratory control spike does not meet the recovery criteria specified in Appendix B, the results of all QC performed with the samples will be evaluated by the analyst. Corrective actions include re-extraction of the samples or reanalysis of the extracts.

4. Sample matrix spike recoveries should fall within the Laboratory Control limits (see appendix B). If a matrix spike recovery fails this criteria, the recovery of the other spiked sample in the MS/MSD pair should be evaluated. If recovery failures are duplicated then the sample matrix is suspected as the problem and the data should be flagged and the failures discussed in the sample narrative. The LCS recoveries can be used to verify that the method was acceptable for the analysis in a clean matrix.

Note: The Aroclor(s) spiked and/or spike amounts may be adjusted when prior knowledge of the type or concentration of Aroclor(s) present in the sample matrix is known, or to comply with project workplans.

Appendix A
DETECTION LIMITS
for PCB's

Aroclor	En Chem[a] Detection Limit Water(µg/L)	En Chem Reporting Limit Water(µg/L)	En Chem[a] Detection Limit Soil (ug/kg)	En Chem[a] Detection Limit Biota(ug/kg)	En Chem Reporting Limit Soil & Biota(ug/kg)
AR1016	0.33	1.0	10	12	50
AR1221	0.33	1.0	10	12	50
AR1232	0.33	1.0	10	12	50
AR1242	0.33	1.0	10	12	50
AR1254	0.33	1.0	10	12	50
AR1260	0.33	1.0	10	12	50

[a] Method Detection Limit determination, USEPA 40CFR Pt.136, App.B, 1988. Method detection limits are updated periodically, the values currently in use may differ slightly from those published.

Appendix B

MS/MSD
QUALITY CONTROL LIMITS[a]
for PCB's

	Water % Rec.	Soil % Rec.	Biota % Rec.
AR1260	(58-124)	(63-129)	(63-129)

LCS
QUALITY CONTROL LIMITS[a]
for PCB's

	Water % Rec.	Soil % Rec.	Biota % Rec.
AR1260	(69-131)	(64-117)	(64-117)

[a]Limits derived from sample analyses, mean value ± 3SD. Control limits are updated periodically, the values currently in use may differ slightly from those shown above. Biota limits are based on soil recoveries and are advisory only.

Note: LCS and MS/MSD limits based on 1260 are being developed. These limits are based on AR1254 spiking, but should be applicable for use in the interim.

SURROGATE
LABORATORY CONTROL LIMITS[a]
for PCB's

	Water % Rec.	Soil % Rec.	Biota % Rec.
Surrogates			
Decachlorobiphenyl	(DL-148)	(60-155)	(60-155)
Tetrachloro-m-xylene	(52-134)	(41-148)	(41-148)

[a] Limits derived from sample analyses, mean value ± 3SD. Control limits are updated periodically, the values currently in use may differ slightly from those shown above. Biota limits are based on soil recoveries are advisory only.

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